PATENT ABSTRACTS OF JAPAN

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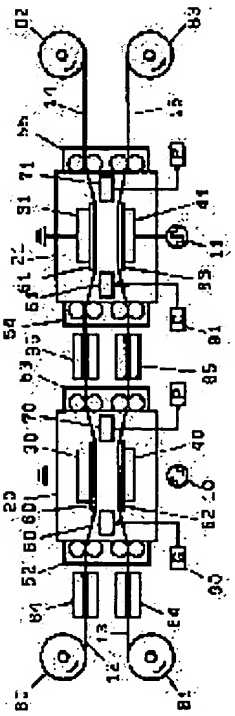
(54) MANUFACTURE OF SURFACE TREATED ARTICLE

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a manufacturing method of a surface-treated article in which the surface-treated article excellent in adhesivity of a thin film to a substrate can be efficiently under the pressure in the vicinity of the atmospheric pressure without any excessive investment on facilities, and deposited substances by the plasma processing are small in quantity.

SOLUTION: In a manufacturing method of surface treated articles 14, 15, processing gases 90, 91 are introduced at the pressure close to the atmospheric pressure between electrodes 30/40 and 31/41 opposite to each other in which solid dielectric materials 60-63 are installed on at least one set of surfaces opposite to each other, the discharge plasma is generated by applying the pulsed electric field to the electrodes 30/40 and 31/41 opposite to each other, and substrates 12, 13 provided between the electrodes 30/40 and 31/41 opposite to each other are plasma-processed. Two substrates 12, 13 are closely attached to the electrodes 30/40 and 31/41 opposite to each other or the solid dielectric materials 60-63, and the processing gases 90, 91 are continuously introduced between two substrates 12, 13.



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TI - MANUFACTURE OF SURFACE TREATED ARTICLE
IN - BESSHO TOMOYUKI;YUASA MOTOKAZU
PA - SEKISUI CHEMICAL CO LTD
IC - C23C16/515 ; C08J7/00 ; C23C16/505 ; C08L101/00

TI - Surface treating e.g. antistatic film, involves introducing gas between substrates and contacting with counter electrodes or solid dielectric between electrodes
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PA - (SEKI) SEKISUI CHEM IND CO LTD
IC - C08J7/00 ;C08L101/00 ;C23C16/505 ;C23C16/515
AB - JP2000212753 NOVELTY - Gas for process (90,91) is introduced continuously between two sheet-like base materials (12,13) and base materials are contacted with counter electrodes (30,40 and 31,41) or solid dielectric (60-63) which respectively and mutually oppose each other, between counter electrodes.
- DETAILED DESCRIPTION - Electric field is impressed between counter electrodes at atmospheric pressure, thereby discharge plasma is generated and plasma treatment of base materials is carried out and plasma treated base material is provided as surface treated goods (14,15).
- USE - For manufacturing various functional films such as anti-reflecting coating membrane, optical permselective membrane, infrared ray reflecting film, antistatic film, electromagnetic wave seal film and semiconductor device material.
- ADVANTAGE - The surface treated good which excels in adhesion of thin film and base material is manufactured easily, efficiently and inexpensively. The formation of sediment on the material during the plasma treatment is eliminated. The need of large-sized exhaust gas device for the process is eliminated. The feeding and taking out of raw material and the product from the apparatus becomes easier.
- DESCRIPTION OF DRAWING(S) - The figure shows apparatus for manufacturing surface treated goods.

- Sheet-like base materials 12,13
- Surface treated goods 14,15
- Counter electrodes 30,40 and 31,41
- Solid dielectric 60-63
- Gas for process 90,91
- (Dwg.3/4)

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- SOLUTION: In a manufacturing method of surface treated articles 14, 15, processing gases 90, 91 are introduced at the pressure close to the atmospheric pressure between electrodes30/40 and 31/41 opposite to each other in which solid dielectric materials 60-63 are installed on at least one set of surfaces opposite to each other, the discharge plasma is generated by applying the pulsed electric field to the electrodes 30/40 and 31/41 opposite to each other, and substrates 12, 13 provided between the electrodes 30/40 and 31/41 opposite to each other are plasma-processed. Two substrates 12, 13 are closely attached to the electrodes 30/40 and 31/41 opposite to each other or the solid dielectric materials 60-63, and the processing gases 90, 91 are continuously introduced between two substrates12, 13.

SI - C08L101/00

I - C23C16/515 ;C08J7/00 ;C23C16/505

* NOTICES * JP 2000-212753

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] this invention relates to the manufacture method of a surface treatment article.
[0002]
[Description of the Prior Art] Although the base material which consists of plastics, a metal, paper, fiber, etc. is widely used as home use and an industrial use material, if specific functions, such as an electrical property, an optical property, and a mechanical characteristic, are given to the front face, the use is expanded further and it comes to have big added value.
[0003] As a method of manufacturing the surface treatment article which comes to carry out the laminating of the thin film which gave the specific function to the front face of the above base materials, a vacuum deposition method, the sputtering method, the ion beam method, the ion plating method, the plasma CVD method using the glow discharge under reduced pressure, etc. are learned. However, each of these methods is performed by the vacuum system, large-scale facilities, such as a vacuum chamber and a large-sized vacuum pump, are required for them, and there are various kinds of limitations in manufacture.
[0004] In order to form a thin film in the front face of a long base material by the vacuum system, two kinds, a batch method and a continuous method, are in manufacture. In a batch method, thin film formation is performed by reduced pressure and the closed system, the roll which wound the base material around the long picture is put into a vacuum chamber, and a thin film is formed by the front face, beginning to roll a base material from a roll in this. By this method, vacuous release and vacuous formation must be repeated for every carrying in of a raw material or taking out of a product, and with the size of a facility, since a limitation appears in the capacity of the diameter of a base-material roll, a thin film raw material, etc., productive efficiency also becomes bad.
[0005] In a continuous method, in order to acquire a reduced pressure state, a differential-pumping method is used, and it exhausts gradually down to reduced pressure from atmospheric pressure, and a thin film is formed all over the space which held continuously the degree of vacuum required for membrane formation of a thin film. Although this method is easy for carrying in and a raw material supplement of a roll base material, since it is necessary to exhaust beyond the inflow of the air into a thin film deposition system, and to hold a degree of vacuum, a mass vacuum pump is needed and growing gigantic of a facility is not avoided.
[0006] Moreover, when giving two or more functions to one base material or adding a more advanced function, the attempt which carries out the laminating of two or more sorts of thin films is made. However, when forming a multilayer industrially, in order to have to repeat the cycle of release of the membrane formation-vacuum of a vacuous formation-thin film for every kind of layer in a batch method, it is very inefficient and is not realistic. Moreover, in a continuous method, a large-scale facility is required also of a monolayer, and introduction of the process of multilayer formation is difficult. Furthermore, correspondence of a little variety was difficult for the continuous method on plant-and-equipment investment, and the correspondence to the use which adds a specific function to a base material separately etc. was very difficult.
[0007] A proposal various in the method of manufacturing the above surface treatment articles is made. in JP,2-181701,A and a ****** No. 518202 [three to] official report Although the method of

controlling the degree of incident angle of an electron gun and the angle of a vacuum evaporationo roll and the source of vacuum evaporationo, and forming a cascade screen on the surface of a base material in a vacuum deposition method is proposed The batch method had to be adopted having consented to the very inefficient thing, since plant-and-equipment investment became excessive too much for carrying out by there being no change in the continuous method using the differential-pumping method.

[0008]

[Problem(s) to be Solved by the Invention] Then, while this invention persons generate electric discharge plasma by introducing the gas for processing between the counterelectrodes by which the solid dielectric was installed in one [at least] opposite side, and impressing the electric field pulse-ized between the pressure near the atmospheric pressure, nothing, and the counterelectrode, the manufacture method of the surface treatment article which carries out plasma treatment of the base material prepared between the aforementioned counterelectrodes is proposed (Japanese-Patent-Application-No. 10-No. 45393 specification). However, in the above-mentioned method, the base material was prepared on one electrode and its productive efficiency was inadequate. Moreover, the sediment by plasma treatment adhered to the electrode side in which the base material is not prepared, and the electrode needed to be cleaned to whenever [the].

[0009] the technical problem of the above [this invention] -- solving -- the bottom of the pressure near the atmospheric pressure -- and it aims at offering the manufacture method of a surface treatment article that do not need excessive plant-and-equipment investment, but manufacture efficiently the surface treatment article excellent in the adhesion of a thin film and a base material, and there are few sediments by plasma treatment and they end

[0010]

[Means for Solving the Problem] The manufacture method (henceforth a "this invention") of a surface treatment article according to claim 1 While generating electric discharge plasma by introducing the gas for processing between the counterelectrodes by which the solid dielectric was installed in one [at least] opposite side, and impressing the electric field pulse-ized between the pressure near the atmospheric pressure, nothing, and the counterelectrode It is the manufacture method of the surface treatment article which carries out plasma treatment of the base material prepared between the aforementioned counterelectrodes, and the base material of two sheets is stuck to the counterelectrode or solid dielectric which confronted each other, respectively, and the gas for processing is continued and introduced between the base materials of two sheets.

[0011] In this invention, the bottom of the pressure near the atmospheric pressure means the bottom of the pressure of 13.3-106.4kPa, pressure regulation is easy, and the range of 93.1-103.74kPa to which equipment becomes simple is desirable.

[0012] Under the pressure near the atmospheric pressure, shifting to an arc discharge state in an instant is known except specific gas, such as helium and a ketone, without holding the stable plasma electric discharge state. However, if the pulse-ized electric field are impressed, before shifting to arc discharge, electric discharge can be stopped, and it realizes, and the cycle of starting electric discharge again can be stabilized and can generate electric discharge plasma.

[0013] According to the method of impressing the pulse-ized electric field in this invention, it is possible to generate electric discharge plasma regardless of the kind of gas which exists all over plasma generating space. Although it was indispensable to have performed processing using electric discharge plasma also under well-known low voltage conditions conventionally within the airtight container intercepted from the open air under a specific gas atmosphere, according to this invention, an open system or the low airtight system of the grade which prevents a free gaseous spill can also be carried out, and the high-density plasma state can be realized.

[0014] In this invention, the build up time of field strength of the electric field to impress is desirable inkV [1-100 //cm] 100 or less microseconds. By impressing the pulse electric field which have a steep standup, the gas molecule which exists all over plasma generating space is because it excites efficiently. It is difficult to ionize efficiently the molecule which excites to level with the higher molecule already ionized when excitation of a molecule small [of the molecule which is equivalent to supplying gradually the energy which has the size from which impressing pulse electric field with a late standup differs, and is first ionized by low energy i.e., the first ionization potential,] takes

place preferentially and energy high next is supplied, and exists all over plasma generating space. On the other hand, according to the pulse electric field whose build up time is 100 or less microseconds, it is equivalent to giving energy to the molecule which exists all over space all at once, the absolute number of the molecule in the state where it ionized in space increases, and plasma density becomes a bird clapper highly. It can do and the high-density plasma state can be realized.

[0015] In this invention, processing takes time too much as the field strength of the electric field to impress is less than 1 kV/cm, and if 100 kV/cm is exceeded, it will become easy to generate arc discharge. In addition, the above-mentioned field strength says what **(ed) the value of the peak-peak of not an effective voltage but the voltage impressed to inter-electrode in inter-electrode distance.

[0016] When it installs a solid dielectric in one side of the above-mentioned electrode, the part which electric discharge plasma generates is the space between solid dielectrics between a solid dielectric and an electrode, when a solid dielectric is installed in the both sides of the above-mentioned electrode.

[0017] As an electrode, what consists of alloys, such as metal simple substances, such as copper and aluminum, stainless steel, and brass, an intermetallic compound, etc. is mentioned, for example. In order to avoid generating of the arc discharge by electric-field concentration, as for a counterelectrode, it is desirable that it is the structure where the distance between counterelectrodes serves as abbreviation regularity. As electrode structure of fulfilling this condition, an parallel monotonous type, a hyperboloid opposite monotonous type, coaxial-circles telescopic structure, etc. are mentioned. Since there is a possibility that arc discharge may occur at the end that an electrode edge is sharp, as for an edge, it is desirable to have carried out taper processing.

[0018] As a solid dielectric, it installs in one side or the both sides of an opposite side of an electrode. Under the present circumstances, a solid dielectric and the electrode of the side installed stick, and are wearing the opposite side of the touching electrode completely. If there is a part which electrodes counter directly, without being covered by the solid dielectric, arc discharge will arise from there.

[0019] As a solid dielectric, multiple oxides, such as metallic oxides, such as plastics, such as a polytetrafluoroethylene and a polyethylene terephthalate, glass, a silicon dioxide, an aluminum oxide, a zirconium dioxide, and a titanium dioxide, and a barium titanate, etc. are mentioned, for example.

[0020] Although the shape of the shape of a sheet and a film has as the configuration of a solid dielectric, it is desirable that thickness is 0.05-4mm. The high voltage is taken to generate electric discharge plasma, if too thick, if too thin, dielectric breakdown will happen at the time of voltage impression, and arc discharge will occur.

[0021] Moreover, as for a solid dielectric, it is desirable that specific inductive capacity is two (bottom of the 25 degreeC environment, following **) or more. Specific inductive capacity can mention a polytetrafluoroethylene, glass, the film that consists of a metallic oxide as an example of two or more dielectrics, for example. Furthermore, in order to be stabilized and to generate high-density electric discharge plasma, it is desirable that specific inductive capacity uses ten or more fixed dielectrics. Although especially the upper limit of specific inductive capacity is not limited, about 18,500 thing is known for an actual material. It is desirable for specific inductive capacity to consist of a metallic-oxide thin film mixed with 5 - 50 % of the weight of oxidization titanium and 50 - 95 % of the weight of aluminum oxides or a metallic-oxide thin film containing a zirconium oxide as ten or more solid dielectrics, and to use that whose thickness of the thin film is 10-1000 micrometers.

[0022] Although an inter-electrode distance is determined in consideration of the purpose using the thickness of a solid dielectric, the size of applied voltage, and plasma etc., it is desirable that it is 1-50mm. In less than 1mm, if it is difficult for an inter-electrode distance to be too small and to prepare a base material on each electrode and it exceeds 50mm, it will become difficult to generate uniform glow discharge plasma.

[0023] Moreover, in this invention, by passing a base material in succession between the counterelectrodes which adjoined two or more sets and were prepared, a thin film of the same kind or of a different kind makes it deposit continuously one by one, and can manufacture a surface

treatment article for each class. In this case, two or more sets of counterelectrodes adjoin, and are arranged, and it is carried out in the equipment with which the solid dielectric is installed in one [at least] opposite side of this counterelectrode. Therefore, the electric discharge plasma treatment equipment of each smallness unit of this invention does not need to have the same arrangement of the solid dielectric of all counterelectrodes, if the above-mentioned conditions are satisfied.
[0024] In this case, the field where the counterelectrode of each class is contained constitutes the electric discharge plasma treatment equipment of the small unit which became independent, respectively, it is supplied so that the gas for processing may serve as a pressure near the atmospheric pressure at this equipment, and by the well-known method, a base material is run the space between counterelectrodes continuously, and is introduced into the electric discharge plasma treatment equipment of the following small unit one by one.
[0025] The example of a pulse-voltage wave is shown in drawing 1 . A wave (A) and (B) are [a square wave type and the wave (D) of an impulse type and a wave (C)] become [irregular] type waves. Although voltage impression mentioned what is the repeat of positive/negative to drawing 1 , you may use the so-called wave of the piece sinuate which impresses voltage to a positive or negative polarity [one of] side.
[0026] Although the pulse-voltage wave in this invention is not limited to the wave mentioned here, ionization of the gas in the case of plasma generating is efficiently performed, so that the build up time of a pulse is short. When the build up time of a pulse exceeds 100 microseconds, an electric discharge state will become being easy to shift to an arc unstable, and it will become impossible to expect the high-density plasma state by pulse electric field. Moreover, although the quicker one of build up time is good, it is difficult for the equipment which has the field strength of the size which is the grade which plasma generates in an ordinary pressure, and is made to generate electric field with quick build up time to have restrictions, and to realize the pulse electric field of the build up time for less than 40ns actually. 50ns - 5 microseconds of build up time are more desirable. In addition, build up time here means time for voltage change to be positive continuously.
[0027] Moreover, the falling time of pulse electric field also has a steep desirable thing, and it is desirable that it is the same time scale for 100 or less microseconds as build up time. Although it changes also with pulse electric-field generating technology, by the power unit used in the example of this invention, it falls with build up time and time can set it as the same time, for example.
[0028] Furthermore, you may become irregular using pulse shape, build up time, and the pulse from which frequency differs. Moreover, in impression of a pulse voltage, you may superimpose a direct current.
[0029] As a power supply used for impression of such a pulse voltage, the thing of a publication is used [Japanese Patent Application No. / No. 186314 / nine to] /, for example.
[0030] Setting to the electric discharge obtained by the above-mentioned method, the discharge current density between counterelectrodes is 0.2 - 300 mA/cm2. Being made is desirable.
[0031] As for the pulse-ized electric field, in this invention, it is desirable that 0.5-100kHz and pulse duration are made for frequency with 1 - 1000 microseconds.
[0032] Since plasma density is low, the frequency of pulse electric field requires time for processing too much, as it is less than 0.5kHz, and if it exceeds 100kHz, arc discharge will become easy to generate it. More preferably, it is 1kHz or more and processing speed can be greatly raised by impressing the pulse electric field of such high frequency.
[0033] Moreover, the pulse duration in the above-mentioned pulse electric field will become easy to shift to arc discharge, if electric discharge becomes being less than 1 microsecond with an unstable thing and it exceeds 1000 microseconds. It is 3 microseconds - 200 microseconds more preferably. Here, although one pulse duration has shown the example in drawing 2 , it means the time in the pulse electric field which consist of a repeat of ON and OFF for a pulse to continue. By intermittence type pulse like drawing 2 (a), although pulse duration is equal to pulse width time, unlike pulse width time, in the pulse of a wave like drawing 2 (b), time including two or more of a series of pulses is said.
[0034] Furthermore, in order to stabilize electric discharge, it is desirable to have the OFF time continued for at least 1 microsecond in 1ms of charging time values. When the above-mentioned discharge current density means the value which **(ed) current value which flows to inter-electrode

by electric discharge in the area of the direction which intersects perpendicularly with the flow direction of the current in discharge space and an parallel monotonous type thing is used as an electrode, it is equivalent to the value which **(ed) the above-mentioned current value in the opposite area. Although pulse-like current flows in this invention in order to form pulse electric field in inter-electrode, the value which **(ed) the maximum of the pulse current, i.e., peak to peak value, in the above-mentioned area in this case is said.

[0035] 0.2 which it is shown clearly by research of this invention persons that it is the value to which discharge current density influences manufacture of a surface treatment article reflecting plasma density, and described above inter-electrode discharge current density in the glow discharge under the pressure near the atmospheric pressure as shown below - 300 mA/cm2 By considering as the range, uniform electric discharge plasma is generated and the manufacture result of a good surface treatment article can be obtained.

[0036] As a base material used for this invention, plastics, such as polyethylene, polypropylene, polystyrene, a polycarbonate, a polyethylene terephthalate, a polyphenylene ape fight, a polyether ether ketone, a polytetrafluoroethylene, and acrylic resin, glass, a ceramic, a metal, etc. are mentioned, for example. Especially as a configuration of a base material, although not limited, in processing continuously, it is suitable for long picture type base materials, such as the shape of the shape of a tabular and a film, and a pipe.

[0037] Although the above-mentioned base material may be fixed and prepared in an electrode or a solid dielectric by the batch type, it is desirable on productive efficiency to make it run an electrode top continuously.

[0038] In this invention, the laminating of arbitrary thin films is possible by selection of the gas (it is hereafter called the gas for processing) which exists not only in the metallic element content gas mentioned later but in electric discharge plasma generating space.

[0039] As gas for processing, by using fluorine content compound gas, a fluorine content machine can be made to be able to form in a base-material front face, surface energy can be made low, and a water-repellent front face can be obtained.

[0040] Especially as a fluorine element content compound, although not limited, it is desirable to use fluorine-carbon compounds which do not generate the hydrogen fluoride which is harmful gas, such as 8 6 fluoride [propylene] (CF3CFCF2), cyclobutane, etc. fluoride (C4F8), from a viewpoint on safe.

[0041] Moreover, a hydrophilic polymerization film can also be made to deposit in a molecule by processing under the atmosphere of the monomer which has a hydrophilic radical and a polymerization nature unsaturated bond. As the above-mentioned hydrophilic radical, hydrophilic radicals, such as a hydroxyl group, a sulfonic group, a sulfonate machine, the 1st class, the 2nd class or the 3rd class amino group, an amide group, a quarternary-ammonium-salt machine, a carboxylic-acid machine, and a carboxylate machine, etc. are mentioned. Moreover, even if it uses the monomer which has a polyethylene-glycol chain, a hydrophilic polymerization film can be deposited similarly.

[0042] As the above-mentioned monomer, acrylic-acid, methacrylic-acid, acrylamide, methacrylamide, N, and N-dimethyl acrylamide, acrylic-acid sodium, methacrylic-acid sodium, an acrylic-acid potassium, a methacrylic-acid potassium, styrene sulfonic-acid sodium, allyl alcohol, an allylamine, polyethylene-glycol dimethacrylate ester, polyethylene-glycol diacylic ester, etc. are mentioned, and these at least one sort can be used.

[0043] If the gas for processing introduced in this invention uses the thing containing metallic element content gas, the surface treatment article with which the oxide film of the used metallic element was formed in the base-material front face can be obtained.

[0044] An electric discharge state cannot be easily stabilized by the atmosphere containing such metallic element content gas, and unless it is based on the method using the electric field by which this invention was pulse-ized, it cannot process. As the above-mentioned metal, for example aluminum, As, Au, B, Bi, Sb, calcium, Cd, Cr, Co, Cu, Fe, Ga, germanium, Hg, Hf, In, Ir, Li, Mg, Mn, Mo, Na, nickel, P, Pb, Po, Pt, Rh, Metals, such as Se, Si, Sn, Ta, Te, Ti, V, W, Y, Zn, and Zr, are mentioned, and the gas for processing, such as a metal organic compound, a metal-halogenated compound, metal-hydride, a metal-halogenated compound, and a metal alkoxide, is mentioned as gas

containing this metal.
[0045] When it specifically explains taking the case of the case where a metal is Si, a tetramethylsilane [Si (CH3)4], Organometallic compound;4 silicon fluorides, such as dimethylsilane [Si(CH3)2H2] and a tetraethyl silane [Si (C2H5)4] (SiF4), Metal halogenated compounds, such as four silicon chlorides (SiCl4) and two silicon chlorides (SiH2Cl2); A mono silane (SiH4), Metal hydride, such as a disilane (SiH3SiH3) and trishiran (SiH3SiH2SiH3); A tetramethoxy silane [Si (OCH3)4], Metal alkoxides, such as a tetrapod ethoxy silane [Si (OC2H5)4], etc. are mentioned, and these at least one sort including other metals can be used if needed. In the above-mentioned metal content gas, in consideration of safety, what does not have danger, such as ignition and explosion, in the ordinary temperature of a metal alkoxide metallurgy group halogenated compound etc. and the atmosphere is desirable, and a metal alkoxide is suitably used from the point of generating of corrosive and harmful gas.
[0046] What is necessary is just to introduce into discharge space through a vaporizer, if it has the shape of a liquid and a solid-state, although it can introduce into discharge space as it is, if the above-mentioned metal content gas is a gas.
[0047] It is more desirable than an atmosphere gas independent [the viewpoint of economical efficiency and safety to / above-mentioned / for processing] to process in the atmosphere thinned with dilution gas. As dilution gas, rare gas, such as helium, neon, an argon, and a xenon, nitrogen gas, etc. are mentioned, and these at least one sort is used, for example. Moreover, when using dilution gas, as for the rate of the gas for processing, it is desirable that it is 0.01 to 10 volume %.
[0048] In addition, it is advantageous, when the way of the compound which has many electrons as a controlled atmosphere (gas for processing) raises plasma density and high-speed processing is performed, as mentioned above. However, an argon or nitrogen is easy to receive and suitable at a cheap point.
[0049] In this invention, the gas for processing is continued and introduced between the base materials of two sheets prepared by sticking the gas for processing on a counterelectrode or a solid dielectric between the above-mentioned counterelectrodes. In this case, a gas supply machine is formed so that the gas for processing may be introduced between the base materials of two sheets, and the gas for processing is continuously introduced towards a base material from this gas supply machine.
[0050] As for the above-mentioned base material, it is desirable to make it run an electrode top continuously as mentioned above. In case it is made to run continuously, the kind of gas for processing introduced into the opposite above-mentioned continuation target should just supply gas of the same kind continuously from a gas supply machine to form one kind of thin film in a base material, and it should just supply the gas of another kind from two sets of gas supply machines to form the thin film of two or more kinds.
[0051] The method of introducing the gas for processing introduced between counterelectrodes in this invention by the well-known method, for example, blowing off the gas for processing with the gas supply vessel of the shape of a slit or a nozzle, the method of preparing the hole which supplies the gas for processing towards the request to the electrode which counters a base-material processing side, and blowing off this, a pump, a blower, and a blower are used, and the method of supplying and circulating etc. is mentioned to inter-electrode.
[0052] In this invention, it is also desirable to improvement in the adhesion of a base material, a thin film, or thin films to carry out plasma treatment to the field where the laminating of a base material or at least one sort of thin films was carried out beforehand.
[0053] Although the atmosphere at the time of carrying out plasma treatment beforehand will not be limited especially if the above-mentioned base material and a thin film are not degraded remarkably, from a viewpoint of economical efficiency and safety, rare gas, such as helium, neon, an argon, and a xenon, nitrogen gas, etc. are mentioned, and these at least one sort is used, for example.
[0054] Since a process is not stabilized in order that electric discharge may arc-ize, if too high [when the applied voltage at the time of carrying out plasma treatment beforehand is too low, it has little improvement in the adhesion of a base material, a thin film, or thin films, and], in argon atmosphere, 1-2kV is 1.2-1.7kV desirable still more preferably, and 6-11kV is 7-8.5kV desirable still more preferably in nitrogen atmosphere.

[0055] Moreover, since plasma density will become high, a base material or a thin film will be deleted flat and smooth, if too high [when the frequency at the time of carrying out plasma treatment is too low, it has little improvement in the adhesion of a base material, a thin film, or thin films, and] and improvement in the adhesion of a base material, a thin film, or thin films decreases, in argon atmosphere or nitrogen atmosphere, 1-8kHz is 2-4kHz desirable still more preferably.
[0056] Furthermore, when it is too short, it has little improvement in the adhesion of a base material, a thin film, or thin films, and if too long, since a base material or a thin film is deleted flat and smooth and the improvement of required for plasma treatment time in the adhesion of a base material, a thin film, or thin films will decrease, in argon atmosphere or nitrogen atmosphere, 5-20sec is desirable [time].
[0057] (Operation) By the manufacture method of the surface treatment article of this invention introducing the gas for processing between the counterelectrodes by which the solid dielectric was installed in one [at least] opposite side, and impressing the electric field pulse-ized between the pressure near the atmospheric pressure, nothing, and the counterelectrode While generating electric discharge plasma, it is the manufacture method of the surface treatment article which carries out plasma treatment of the base material prepared between the aforementioned counterelectrodes. In the state where stuck the base material of two sheets to the counterelectrode or solid dielectric which confronted each other, respectively, the gas for processing was introduced between counterelectrodes since the gas for processing is continued and introduced between the base materials of two sheets, and it was made with the pressure near the atmospheric pressure The pulse-ized electric field are impressed, by impressing predetermined pulse electric field to a counterelectrode, the electric discharge plasma depending on the aforementioned gas for processing occurs, and a thin film is formed in the base material of two sheets prepared into this electric discharge plasma at the same time it generates the stable high-density plasma.
[0058] Moreover, since plasma treatment can be performed by the ordinary pressure, processing is performed under the pressure near the atmospheric pressure in equipment. The large-scale exhaust like [that it should just change the seal of the inlet of a base material and the exhaust port into the secret state of a grade where the leakage of a gas can be permitted] the processing performed by the vacuum system is not needed. Therefore, supply of a base material, change of a base material, and change of gas composition can be performed freely, and can manufacture various kinds of surface treatment articles economically.
[0059] Furthermore, a thin film can be formed between short time, without arc discharge occurring, while the gas molecule which exists all over plasma generating space when the voltage build up time of the electric field pulse-ized [above] takes and field strength takes 100 or less microseconds for 1 - 100 kV/cm excites efficiently.
[0060]
[Embodiments of the Invention] The form of the operation of this invention to the following is explained in detail, referring to a drawing. Drawing 3 is the ** type view showing an example of the equipment used for the manufacture method of the surface treatment article of this invention. As shown in drawing 3 , the equipment used for this invention It mainly consists of the high-voltage pulse power supply sections 10 and 11, electric discharge plasma treatment equipments 20 and 21, **** rolls 80 and 81, and taking over rolls 82 and 83. Each electric discharge plasma treatment equipments 20 and 21 consist of an parallel monotonous type counterelectrode (the up electrodes 30 and 31, lower electrodes 40 and 41), the gas supply sections 50 and 51 for processing, solid dielectrics 60, 61, 62, and 63, and the gas discharge sections 70 and 71 for processing.
[0061] Moreover, the up electrodes 30 and 31 are equipped with 60 and 61, and, as for the solid dielectric, the lower electrodes 40 and 41 are equipped with 62 and 63.
[0062] Various kinds of gas 90 and 91 for processing between the counterelectrodes (namely, 30/40, 31/41) of the electric discharge plasma treatment equipments 20 and 21 under the pressure near the atmospheric pressure Arbitrary kinds are chosen and introduced according to the purpose, and the pulse-ized electric field by above-mentioned conditions are impressed to each electrode. The electric discharge plasma according to the kind of gas for processing is generated. to this at the solid dielectrics 60 and 61 of the up electrodes 30 and 31 a base material 12 A base material 13 is stuck to the solid dielectrics 62 and 63 of the lower electrodes 40 and 41, respectively, and various kinds of

thin films accumulate on the undersurface of a base material 12, and the upper surface of a base material 13, respectively.
[0063] As described above, the kind of gas 90 and 91 for processing introduced into each electric discharge plasma treatment equipments 20 and 21 changes with purposes, and even if, and it is different species, it is not cared about.
[0064] Heating and cooling systems 84 and 85 are adjacently formed in each electric discharge plasma treatment equipments 20 and 21, and base materials 12 and 13 have come be made to desired temperature. Of course, heating and a cooler style are included in the electric discharge plasma treatment equipments 20 and 21, and it does not matter as a temperature control being possible.
[0065] The seal of the electric discharge plasma treatment equipments 20 and 21 is carried out by the seal mechanisms 52, 53, 54, and 55, and they supply the gas 90 and 91 for after treatment which changed the inside of electric discharge plasma treatment equipment 20 and 21 into the reduced pressure state by vacuum pump P at the abbreviation vacua.
[0066] The gas which is supplied from the gas supply sections 50 and 51 for processing, and exists in throughout [counterelectrode (namely, 30/40, 31/41)] forms a laminar flow between a base material 12 and 13, and it is desirable that the rate of flow is almost uniform covering the processing width of face of a base material.
[0067] Drawing 4 shows an example of the gas supply sections 50 and 51 for processing, (A) is the cross section and (B) is the A-A cross section.
[0068] While the gas inlet 56 by which the gas supply pipe G is connected to the end section of the longitudinal direction of the direct rectangle-like gas supply section 50 for processing is formed By the ability forming [preparing two loculus in a longitudinal direction, and] the 1st room of a cam plate 14 on the diagonal line of 57 so that the 1st room may counter 57 in the gas introduction direction Form the partition which becomes so narrow that it keeps away from a gas inlet 56, and the reactant gas introduced from the gas inlet 56 is turbulent-flow-ized. abbreviation equalization of the density within the partition is carried out -- making -- the rate of flow -- abbreviation -- after deflecting the direction at the same time it considers as a uniform thing, it has the structure which rectifies gas and blows off from the stoma group 15 of uniform a large number prepared near the edge of 57 the 1st room
[0069] It is constituted so that can prepare 58 [room / 2nd], the gas which formed the slit 25 of uniform width of face near the edge, and came out of the 1st room of the stoma group 15 of 57 may turn around a diaphragm 24 in the 2nd room 58 while arranging the diaphragm 24 with which the gas which came out of the stoma group 15 is introduced and which has the uniform crevice 23 at the end, and it may become a laminar flow from a slit 25 and it may blow off to discharge space. Thereby, the flow of the gas which came out of the stoma group 15 is equalized.
[0070] In addition, as shown in drawing 3 , although the power supply which became independent to each of each electric discharge plasma treatment equipment is being used for the high-voltage pulse power supplies 10 and 11, a common power supply may be used for them.
[0071] moreover -- although the example which makes reduced pressure only the electric discharge plasma treatment equipments 20 and 21, and replaces them by the raw gas in drawing 3 was shown -- the **** rolls 80 and 81, the taking over rolls 82 and 83, and heating and cooling systems 84 and 85 -- all may be made reduced pressure and you may replace by the raw gas
[0072] Moreover, although the example which supplies base materials 12 and 13 from the separate **** rolls 80 and 81 in drawing 3 was shown, before making the **** roll common and introducing into electric discharge plasma treatment equipment, after establishing the cutting means and cutting to required width of face, you may supply so that it may stick to the opposite side of a counterelectrode (or solid dielectric), respectively.
[0073]
[Example] Hereafter, an example is hung up and this invention is explained in more detail. In addition, in the following examples, (the Heiden lab company make, the product made from semiconductor device:IXYS, and part number IXBH40N160-627G) were used as high-voltage pulse power supply sections 10 and 11.
[0074] In the equipment shown in drawing 3 , it considered as the manufacturing installation of a surface treatment article using what has the gas diffuser of the shape of a slit shown in drawing 4 as

the gas supply sections 50 and 51 for processing. In addition, both, the up electrodes 30 and 31 of electric discharge plasma treatment equipment and the lower electrodes 40 and 41 are parallel monotonous type electrodes with a width-of-face 350x length of 150mm made from SUS304, and what coated the opposite side with the aluminum-oxide coat with a thickness of 1.5mm by the spraying process was used for them.

[0075] Base materials 12 and 13 used the polyethylene-terephthalate film (the Toray Industries, Inc. make, tradename "lumiler T50") with a thickness [of 50 micrometers], and a width of face of 300mm, and they supplied it, making it stick to the solid dielectrics 60 and 61 of the up electrodes 30 and 31, and the solid dielectrics 62 and 63 of the lower electrodes 40 and 41, and making it run the upper and lower sides by 0.5 m/min continuously from two **** rolls 80 and 81.

[0076] Subsequently, after setting the inside of electric discharge plasma treatment equipment 20 and 21 to 0.1Torr(s) by vacuum pump P, the nitrogen gas containing the tetrapod ethoxy silane of 0.5 volume % and the oxygen gas of 20 volume % was supplied by both 15SLM(s) from the argon gas which contains tetrapod isopropanal POKISHICHITANETO of 0.5 volume % from the gas supply section 50 for processing, and the gas supply section 51 for processing, and it considered as abbreviation atmospheric pressure.

[0077] subsequently, between the solid dielectrics 60 and 61 of the up electrodes 30 and 31, the solid dielectric 62 of the lower electrodes 40 and 41, and 63 -- the applied voltage of 4kV, the frequency of 6kHz, and pulse-voltage wave: -- plasma treatment was performed in drawing 1 (A), 5 microsecond [of build up time], 20 microsecond [of pulse width], and charging-time-value 20 seconds

[0078] Consequently, it is TiO2 to the front face of base materials 12 and 13. A film and SiO2 The surface treatment article 14 and 15 with which the film was formed was obtained.

[0079] The refractive index of the thin film of the obtained surface treatment article 14 and 15 and thickness were measured using the ellipsomter (the MIZOJIRI OPTICAL Co., Ltd. make, form "BVA-36VW"). Furthermore, the surface treatment article 14 and 15 was arbitrarily cut to A4 edition, and the thickness homogeneity of each thin film was measured at 5mm interval using optical interference formula automatic thickness-measurement equipment (made in NANOMETO Rix Japan, form "M-5100").

[0080] Consequently, TiO2 formed in the surface treatment article 14 and 15 Films were a refractive index 2.13 and 95nm of thickness, and the thickness distribution (R) was **3%. Moreover, SiO2 Films were a refractive index 1.44 and 128nm of thickness, and the thickness distribution (R) was **3%.

[0081] Subsequently, when the reflection factor of the obtained surface treatment article 14 and 15 was measured with the spectrophotometer (the Hitachi, Ltd. make, form "U-3000%), both visible-ray average (wavelength of 400-700nm) reflection factors are 0.2%, and the acid-resisting function was sharply given compared with the polyethylene-terephthalate film (7%). Moreover, the surface treatment article 14 and 15 is 9m2/hr, and processing area became double precision when processing efficiency sticks a base material to the electrode only by the side of one side.

[0082]

[Effect of the Invention] Since it is constituted as mentioned above, it is under the pressure near the atmospheric pressure, and the manufacture method of the surface treatment article of this invention does not need excessive plant-and-equipment investment, but manufactures efficiently the surface treatment article excellent in the adhesion of a thin film and a base material, and has few sediments by plasma treatment, and ends. Therefore, it can use for manufacture of various functional films, such as an antireflection film, an optical permselective membrane, an infrared reflective film, an antistatic film, an electromagnetic wave seal film, and semiconductor-device material, using the manufacture method of this invention.

[0083] Moreover, like the former, since it is not necessary to make the continuation manufacturing installation of the cascade screen of this invention into a reduced pressure system, its large-sized exhaust is unnecessary, and since carrying in and taking out of a raw material and a product become easy, it is very useful from the point of production operation nature and the economical efficiency of a production facility.

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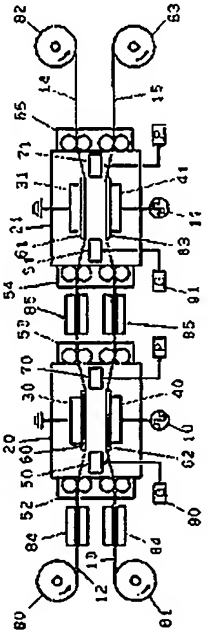
最終頁に続く

(54)【発明の名称】　表面処理品の製造方法

(57)【要約】
【課題】　大気圧近傍の圧力の下で、且つ、過大な設備投資を必要とせず、薄膜と基材との密着性に優れた表面処理品を効率よく製造し、又、プラズマ処理による堆積物が少なくてすむ表面処理品の製造方法を提供する。
【解決手段】　少なくとも一方の対向面に固体誘電体６０～６３が設置された対向電極３０／４０、３１／４１間に処理用ガス９０、９１を導入して、大気圧近傍の圧力となし、対向電極間３０／４０、３１／４１にパルス化された高界を印加することにより、放電プラズマを発生させるとともに、前記対向電極３０／４０、３１／４１間に設けられた基材１２、１３をプラズマ処理する表面処理品１４、１５の製造方法であって、２枚の基材１２、１３を、それぞれ対峙された対向電極３０／４０、３１／４１又は固体誘電体６０～６３に密着させて、２枚の基材１２、１３の間に処理用ガス９０、９１を連続して導入する。



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【特許請求の範囲】

【請求項１】　少なくとも一方の対向面に固体誘電体が設置された対向電極間に処理用ガスを導入して、大気圧近傍の圧力となし、対向電極間にパルス化された電界を印加することにより、放電プラズマを発生させるとともに、前記対向電極間に設けられた基材をプラズマ処理する表面処理品の製造方法であって、２枚の基材を、それぞれ対峙された対向電極又は固体誘電体に密着させて、２枚の基材の間に処理用ガスを連続して導入することを特徴とする表面処理品の製造方法。

【請求項２】　上記パルス化された電界の電圧立ち上がり時間が１００μｓ以下、電界強度が１～１００ｋＶ／ｃｍであることを特徴とする請求項１記載の表面処理品の製造方法。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は表面処理品の製造方法に関する。

【０００２】

【従来の技術】プラスチック、金属、紙、繊維などからなる基材は、家庭用、工業用材料として広く利用されているが、その表面に電気特性、光学特性、機械特性などの特定の機能が付与されれば、その用途が更に拡大され、又、大きな付加価値を有するようになる。

【０００３】上記のような基材の表面に特定の機能を付与した薄膜を積層してなる表面処理品を製造する方法としては、真空蒸着法、スパッタリング法、イオンビーム法、イオンプレーティング法、減圧下でのグロー放電を利用したプラズマＣＶＤ法などが知られている。しかし、これらの方法は、いずれも真空系で行われ、真空チャンバー、大型真空ポンプなど大がかりな設備が必要であり、製造には各種の限界がある。

【０００４】長尺基材の表面に薄膜を真空系で形成するには、製造にバッチ方式と連続方式の２種類がある。バッチ方式に於いては、薄膜形成が減圧・閉鎖系で行われ、基材を長尺に巻いたロールを真空チャンバーに入れ、この中でロールから基材を巻き出しながら表面に薄膜が成膜される。この方式では、原料の投入や製品の搬出ごとに、真空の解除と形成を繰り返さなくてはならなく、設備の大きさにより、基材ロールの直径、薄膜原料などの容量に限界がでるので、生産効率も悪くなる。

【０００５】連続方式に於いては、減圧状態を得るために差動排気方式を用い、大気圧から減圧下へ徐々に排気を行って、薄膜の成膜に必要な真空度を連続的に保持した空間中で薄膜が形成される。この方式は、ロール基材の投入や原料補充は容易であるが、薄膜形成装置内への空気の流入以上に排気を行って真空度を保持する必要があるので、大容量の真空ポンプが必要となり、設備の巨大化は避けられない。

【０００６】又、一つの基材に複数の機能を付与した

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り、より高度な機能を添加する場合は、複数種の薄膜を積層する試みがなされている。しかし、工業的に多層膜を形成する場合は、バッチ方式では、真空の形成－薄膜の成膜－真空の解除のサイクルを、層の種類毎に繰り返さなくてはならないため、極めて非能率的で、現実的でない。又、連続方式では、単層でも大規模な設備が必要であり、多層膜形成のプロセスの導入は困難である。更に、連続方式は、設備投資上、少量多種の対応が困難であり、基材に特定機能を個々に付加する用途への対応などは極めて困難であった。

【０００７】上述のような表面処理品を製造する方法は、種々の提案がなされ、例えば、特開平２－１８１７０１号公報、特表平３－５１８２０２号公報には、真空蒸着法に於いて、電子銃の入射角度や蒸着ロールと蒸着源との角度を制御して、基材の表面に積層膜を形成する方法が提案されているが、差動排気方式を用いた連続方式に変わりはなく、実施するには設備投資が過大となり過ぎるので、極めて非能率的であることを承知しながら、バッチ方式を採用せざるを得なかった。

【０００８】

【発明が解決しようとする課題】そこで、本発明者らは、少なくとも一方の対向面に固体誘電体が設置された対向電極間に処理用ガスを導入して、大気圧近傍の圧力となし、対向電極間にパルス化された電界を印加することにより、放電プラズマを発生させるとともに、前記対向電極間に設けられた基材をプラズマ処理する表面処理品の製造方法を提案している（特願平１０－４５３９３号明細書）。しかし、上記の方法においては、基材は一方の電極上に設けられており、生産効率が不十分であった。また、基材が設けられていない電極側に、プラズマ処理による堆積物が付着し、その度に電極の清掃を行う必要があった。

【０００９】本発明は上記の課題を解決し、大気圧近傍の圧力の下で、且つ、過大な設備投資を必要とせず、薄膜と基材との密着性に優れた表面処理品を効率よく製造し、又、プラズマ処理による堆積物が少なくてすむ表面処理品の製造方法を提供することを目的とする。

【００１０】

【課題を解決するための手段】請求項１に記載の表面処理品の製造方法（以下、「本発明」という）は、少なくとも一方の対向面に固体誘電体が設置された対向電極間に処理用ガスを導入して、大気圧近傍の圧力となし、対向電極間にパルス化された電界を印加することにより、放電プラズマを発生させるとともに、前記対向電極間に設けられた基材をプラズマ処理する表面処理品の製造方法であって、２枚の基材を、それぞれ対峙された対向電極又は固体誘電体に密着させて、２枚の基材の間に処理用ガスを連続して導入するものである。

【００１１】本発明に於いて、大気圧近傍の圧力下とは、１３．３～１０６．４ｋＰａの圧力下を意味し、圧

力調整が容易で．装置が簡便になる９３．１～１０３．７４ｋＰａの範囲が好ましい。

【００１２】大気圧近傍の圧力下では．ヘリウム．ケトン等の特定のガス以外は．安定したプラズマ放電状態が保持されずに．瞬時にアーク放電状態に移行することが知られている。しかし、パルス化された電界を印加すると．アーク放電に移行する前に放電を止め、再び放電を開始するというサイクルが実現し、安定して放電プラズマを発生させることができる。

【００１３】本発明に於けるパルス化された電界を印加する方法によれば、プラズマ発生空間中に存在する気体の種類を問わず放電プラズマを発生させることが可能である。従来より．放電プラズマを利用する処理は．公知の低圧条件下でも、特定のガス雰囲気下でも、外気から遮断された密閉容器内で行うことが必須であったが、本発明によれば．開放系でも．気体の自由な流失を防ぐ程度の低気密系でも実施でき．且つ、高密度のプラズマ状態を実現できる。

【００１４】本発明に於いて、印加する電界の立ち上がり時間が１００μｓ以下．電界強度が１～１００ｋＶ／ｃｍが好ましい。急峻な立ち上がりを有するパルス電界を印加することにより、プラズマ発生空間中に存在する気体分子が、効率よく励起するからである。立ち上がりが遅いパルス電界を印加することは．異なる大きさを有するエネルギーを段階的に投入することに相当し．まず低エネルギーで電離する分子、即ち．第一イオン化ポテンシャルの小さい分子の励起が優先的に起こり．次に高いエネルギーが投入された際には既に電離している分子がより高い準位に励起し．プラズマ発生空間中に存在する分子を効率よく電離することは難しい。これに対して．立ち上がり時間が１００μｓ以下であるパルス電界によれば、空間中に存在する分子に一斉にエネルギーを与えることに相当し、空間中の電離した状態にある分子の絶対数が多くなり、プラズマ密度が高くなることになる。でき、且つ．高密度のプラズマ状態を実現できる。

【００１５】本発明に於いて、印加する電界の電界強度が１ｋＶ／ｃｍ未満であると処理に時間がかかり過ぎ、１００ｋＶ／ｃｍを超えるとアーク放電が発生し易くなる。なお、上記電界強度は実効電圧ではなく、電極間に印加された電圧のピーク－ピークの値を電極間距離で除したものをいう。

【００１６】放電プラズマが発生する部位は、上記電極の一方に固体誘電体を設置した場合は．固体誘電体と電極の間、上記電極の双方に固体誘電体を設置した場合は．固体誘電体同士の間の空間である。

【００１７】電極としては．例えば．銅、アルミニウム等の金属単体．ステンレス．真鍮等の合金、金属間化合物等からなるものが挙げられる。対向電極は、電界集中によるアーク放電の発生を避けるために、対向電極間の距離が略一定となる構造であることが好ましい。この条

件を満たす電極構造としては、平行平板型、双曲面対向平板型、同軸円筒型構造等が挙げられる。電極端部が鋭敏であると、端部でアーク放電が発生する虞があるため．端部はテーパー加工してあることが好ましい。

【００１８】固体誘電体としては、電極の対向面の一方又は双方に設置する。この際、固体誘電体と設置される側の電極が密着し、且つ．接する電極の対向面を完全に覆うようにする。固体誘電体によって覆われずに電極同士が直接対向する部位があると、そこからアーク放電が生じる。

【００１９】固体誘電体としては、例えば、ポリテトラフルオロエチレン、ポリエチレンテレフタレート等のプラスチック、ガラス、二酸化珪素、酸化アルミニウム、二酸化ジルコニウム、二酸化チタン等の金属酸化物、チタン酸バリウム等の複酸化物等が挙げられる。

【００２０】固体誘電体の形状は、シート状でもフィルム状でもよいが．厚みが０．０５～４ｍｍであることが好ましい。厚過ぎると、放電プラズマを発生するのに高電圧を要し、薄過ぎると．電圧印加時に絶縁破壊が起こりアーク放電が発生する。

【００２１】又．固体誘電体は、比誘電率が２以上（２５°Ｃ環境下．以下同）であることが好ましい。比誘電率が２以上の誘電体の具体例としては．例えば．ポリテトラフルオロエチレン、ガラス、金属酸化物からなる膜等を挙げることができる。更に、高密度の放電プラズマを安定して発生させるためには、比誘電率が１０以上の固定誘電体を用いることが好ましい。比誘電率の上限は．特に限定されるものではないが．現実の材料では１８，５００程度のものが知られている。比誘電率が１０以上の固体誘電体としては．酸化チタニウム５～５０重量％．酸化アルミニウム５０～９５重量％で混合された金属酸化物薄膜．又は、酸化ジルコニウムを含有する金属酸化物薄膜からなり、その薄膜の厚みが１０～１０００μｍであるものを用いることが好ましい。

【００２２】電極間の距離は、固体誘電体の厚さ．印加電圧の大きさ．プラズマを利用する目的等を考慮して決定されるが、１～５０ｍｍであることが好ましい。１ｍｍ未満では、電極間の距離が小さ過ぎて、各電極上に基材を設けることが難しく．５０ｍｍを超えると．均一なグロー放電プラズマを発生させることが困難となる。

【００２３】また、本発明に於いて．複数組隣接されて設けられた対向電極間に．基材を連続して通過させることにより、各組毎に同種又は異種の薄膜が順次連続的に堆積させて、表面処理品を製造することができる。この場合．対向電極が複数組隣接して配置され、該対向電極の少なくとも一方の対向面に固体誘電体が設置されている装置に於いて行われる。従って、本発明の各小単位の放電プラズマ処理装置は．上記条件を満足すれば．全ての対向電極の固体誘電体の配置が同一である必要はない。

【００２４】この場合、各組の対向電極が収納されている領域は、それぞれ独立した小単位の放電プラズマ処理装置を構成し、該装置に処理用ガスが大気圧近傍の圧力となるように供給され、基材は公知の方法により、対向電極間の空間を連続的に走行させられ、順次、次の小単位の放電プラズマ処理装置に導入される。

【００２５】図１にパルス電圧波形の例を示す。波形（Ａ）、（Ｂ）はインパルス型、波形（Ｃ）は方形波型、波形（Ｄ）は変調型の波形である。図１には電圧印加が正負の繰り返しであるものを挙げたが、正又は負のいずれかの極性側に電圧を印加する、いわゆる片波状の波形を用いてもよい。

【００２６】本発明に於けるパルス電圧波形は、ここで挙げた波形に限定されないが、パルスの立ち上がり時間が短いほどプラズマ発生の際のガスの電離が効率よく行われる。パルスの立ち上がり時間が１００μｓを超えると、放電状態がアークに移行し易く不安定なものとなり、パルス電界による高密度プラズマ状態を期待できなくなる。又、立ち上がり時間は速い方がよいが、常圧でプラズマが発生する程度の大きさの電界強度を有し、且つ、立ち上がり時間が速い電界を発生させる装置には制約があり、現実的には４０ｎｓ未満の立ち上がり時間のパルス電界を実現することは困難である。立ち上がり時間は、５０ｎｓ～５μｓがより好ましい。尚、ここでいう立ち上がり時間とは、電圧変化が連続して正である時間を意味する。

【００２７】又、パルス電界の立ち下がり時間も急峻であることが好ましく、立ち上がり時間と同様の１００μｓ以下のタイムスケールであることが好ましい。パルス電界発生技術によっても異なるが、例えば、本発明の実施例で使用した電源装置では、立ち上がり時間と立ち下がり時間が同じ時間に設定できる。

【００２８】更に、パルス波形、立ち上がり時間、周波数の異なるパルスを用いて変調を行ってもよい。又、パルス電圧の印加に於いて、直流を重畳してもよい。

【００２９】このようなパルス電圧の印加に使用される電源としては、例えば、特願平９－１８６３１４号に記載のものが使用される。

【００３０】上記の方法により得られる放電に於いて、対向電極間の放電電流密度は、０．２～３００ｍＡ／ｃｍ^{2}となされていることが好ましい。

【００３１】本発明に於いて、パルス化された電界は、周波数が０．５～１００ｋＨｚ、パルス継続時間が１～１０００μｓとなされているのが好ましい。

【００３２】パルス電界の周波数は、０．５ｋＨｚ未満であると、プラズマ密度が低いため処理に時間がかかりすぎ、１００ｋＨｚを超えるとアーク放電が発生し易くなる。より好ましくは、１ｋＨｚ以上であり、このような高周波数のパルス電界を印加することにより、処理速度を大きく向上させることができる。

【００３３】又、上記パルス電界に於けるパルス継続時間は、１μｓ未満であると放電が不安定なものとなり、１０００μｓを超えると、アーク放電に移行し易くなる。より好ましくは、３μｓ～２００μｓである。ここで、一つのパルス継続時間とは、図２中に例を示してあるが、ＯＮ、ＯＦＦの繰り返しからなるパルス電界に於ける、パルスが連続する時間をいう。図２（ａ）のような間欠型のパルスでは、パルス継続時間はパルス幅時間と等しいが、図２（ｂ）のような波形のパルスでは、パルス幅時間とは異なり、一連の複数のパルスを含んだ時間をいう。

【００３４】更に、放電を安定させるためには、放電時間１ｍｓ内に、少なくとも１μｓ継続するＯＦＦ時間を有することが好ましい。上記放電電流密度とは、放電により電極間に流れる電流値を、放電空間に於ける電流の流れ方向と直交する方向の面積で除した値をいい、電極として平行平板型のものを用いた場合には、その対向面積で上記電流値を除した値に相当する。本発明では電極間にパルス電界を形成するため、パルス状の電流が流れるが、この場合にはそのパルス電流の最大値、つまりピーク－ピーク値を、上記の面積で除した値をいう。

【００３５】大気圧近傍の圧力下でのグロー放電では、下記に示すように、放電電流密度がプラズマ密度を反映し、表面処理品の製造を左右する値であることが、本発明者らの研究により明らかにされており、電極間の放電電流密度を前記した０．２～３００ｍＡ／ｃｍ^{2}の範囲とすることにより、均一な放電プラズマを発生して良好な表面処理品の製造結果を得ることができる。

【００３６】本発明に使用される基材としては、例えば、ポリエチレン、ポリプロピレン、ポリスチレン、ポリカーボネート、ポリエチレンテレフタレート、ポリフェニレンサルファイト、ポリエーテルエーテルケトン、ポリテトラフルオロエチレン、アクリル樹脂等のプラスチック、ガラス、セラミック、金属等が挙げられる。基材の形状としては、特に限定されるものではないが、連続して処理を行う場合には、板状、フィルム状、パイプ状など長尺型の基材に適している。

【００３７】上記基材は、バッチ式で電極又は固体誘電体に固定して設けられてもよいが、生産効率上、連続的に電極上を走行させるのが好ましい。

【００３８】本発明に於いて、後述する金属元素含有ガスのみでなく、放電プラズマ発生空間に存在する気体（以下、処理用ガスと呼ぶ）の選択により任意の薄膜の積層が可能である。

【００３９】処理用ガスとしては、フッ素含有化合物ガスを用いることによって、基材表面にフッ素含有基を形成させて表面エネルギーを低くし、撥水性表面を得ることができる。

【００４０】フッ素元素含有化合物としては、特に限定されないが、安全上の観点から、有害ガスであるフッ化

水素を生成しない６フッ化プロピレン（CF_3CFCF_2）、８フッ化シクロブタン（C_4F_8）等のフッ素－炭素化合物を用いるのが好ましい。

【００４１】又、分子内に親水性基と重合性不飽和結合を有するモノマーの雰囲気下で処理を行うことにより、親水性の重合膜を堆積させることもできる。上記親水性基としては、水酸基、スルホン酸基、スルホン酸塩基、１級若しくは２級又は３級アミノ基、アミド基、４級アンモニウム塩基、カルボン酸基、カルボン酸塩基等の親水性基等が挙げられる。又、ポリエチレングリコール鎖を有するモノマーを用いても同様に親水性重合膜を堆積が可能である。

【００４２】上記モノマーとしては、アクリル酸、メタクリル酸、アクリルアミド、メタクリルアミド、Ｎ，Ｎ－ジメチルアクリルアミド、アクリル酸ナトリウム、メタクリル酸ナトリウム、アクリル酸カリウム、メタクリル酸カリウム、スチレンスルホン酸ナトリウム、アリルアルコール、アリルアミン、ポリエチレングリコールジメタクリル酸エステル、ポリエチレングリコールジアクリル酸エステルなどが挙げられ、これらの少なくとも１種が使用できる。

【００４３】本発明に於いて導入される処理用ガスが、金属元素含有ガスを含むものを使用すると、使用した金属元素の酸化皮膜が基材表面に形成された表面処理品を得ることができる。

【００４４】このような金属元素含有ガスを含む雰囲気は放電状態が安定し難く、本発明のパルス化された高昇を用いる方法によらないと処理を行うことができない。上記金属としては、例えば、Ａｌ、Ａｓ、Ａｕ、Ｂ、Ｂｉ、Ｓｂ、Ｃａ、Ｃｄ、Ｃｒ、Ｃｏ、Ｃｕ、Ｆｅ、Ｇａ、Ｇｅ、Ｈｇ、Ｈｆ、Ｉｎ、Ｉｒ、Ｌｉ、Ｍｇ、Ｍｎ、Ｍｏ、Ｎａ、Ｎｉ、Ｐ、Ｐｂ、Ｐｏ、Ｐｔ、Ｒｈ、Ｓｅ、Ｓｉ、Ｓｎ、Ｔａ、Ｔｅ、Ｔｉ、Ｖ、Ｗ、Ｙ、Ｚｎ、Ｚｒ等の金属が挙げられ、該金属を含有するガスとしては、金属有機化合物、金属－ハロゲン化合物、金属－水素化合物、金属－ハロゲン化合物、金属アルコキシド等の処理用ガスが挙げられる。

【００４５】具体的には、金属がＳｉである場合を例にとって説明すると、テトラメチルシラン[$Si(CH_3)_4$]、ジメチルシラン[$Si(CH_3)_2H_2$]、テトラエチルシラン[$Si(C_2H_5)_4$]等の有機金属化合物；４フッ化珪素（SiF_4）、４塩化珪素（$SiCl_4$）、２塩化珪素（SiH_2Cl_2）等の金属ハロゲン化合物；モノシラン（SiH_4）、ジシラン（Si_2H_6）、トリシラン（Si_3H_8）等の金属水素化合物；テトラメトキシシラン[$Si(OCH_3)_4$]、テトラエトキシシラン[$Si(OC_2H_5)_4$]等の金属アルコキシド等が挙げられ、必要に応じて、他の金属を含めこれらの少なくとも１種が使用できる。上記の金属含有ガスに於いて、安全性を考慮して、金属アルコキシドや金属ハロゲン化合物などの高温、大気中で発火、爆発など危険性がないものが好ましく、腐食性、有害ガスの発生の点から、金属アルコキシドが好適に使用される。

【００４６】上記の金属含有ガスが気体であれば、放電空間にそのまま導入することができるが、液体、固体状であれば、気化装置を経て放電空間に導入すればよい。

【００４７】経済性及び安全性の観点から、上記処理用ガス単独の雰囲気よりも、希釈ガスで薄められた雰囲気中で処理を行うことが好ましい。希釈ガスとしては、例えば、ヘリウム、ネオン、アルゴン、キセノン等の希ガス、窒素ガス等が挙げられ、これらの少なくとも１種が使用される。又、希釈ガスを用いる場合、処理用ガスの割合は０．０１～１０体積％であることが好ましい。

【００４８】尚、上述したように、雰囲気ガス（処理用ガス）としては電子を多く有する化合物のほうがプラズマ密度を高め高速処理を行う上で有利である。しかし、アルゴン又は窒素が、入手が容易で、安価である点で好適である。

【００４９】本発明に於いて、上記対向高極間に、処理用ガスを対向電極又は固体誘電体上に密着して設けられた２枚の基材の間に処理用ガスを連続して導入する。この場合、２枚の基材の間に処理用ガスが導入されるようにガス供給器を設け、該ガス供給器から基材へ向けて連続的に処理用ガスを導入する。

【００５０】上記基材は、上述のように連続的に電極上を走行させるのが好ましい。連続して走行させる際、対向上記連続的に導入される処理用ガスの種類は、基材に１種類の薄膜を形成したい場合は、ガス供給器から連続して同種のガスを供給すればよいし、複数の種類の薄膜を形成したい場合は、２台のガス供給器から別種のガスを供給すればよい。

【００５１】本発明に於いて、対向電極間に導入する処理用ガスは、公知の方法で導入でき、例えばスリットやノズル状のガス供給器によって処理用ガスを吹き出す方法、基材処理面に対向する電極に所望の方向に処理用ガスを供給する孔を設けてこれを吹き出す方法、ポンプ、ブロアー、送風機を用いて電極間に供給・循環する方法等が挙げられる。

【００５２】本発明に於いて、基材又は少なくとも１種の薄膜が積層された面に予めプラズマ処理するのも、基材と薄膜、又は、薄膜同士の密着性の向上に好ましい。

【００５３】予めプラズマ処理する際の雰囲気は上記基材及び薄膜を著しく劣化させるものでなければ特に限定されないが、経済性及び安全性の観点から、例えば、ヘリウム、ネオン、アルゴン、キセノン等の希ガス、窒素ガス等が挙げられ、これらの少なくとも１種が使用される。

【００５４】予めプラズマ処理する際の印加高圧は、低すぎると基材と薄膜、又は、薄膜同士の密着性の向上が少なく、高すぎると放電がアーク化するため、プロセス

が安定しないので、アルゴン雰囲気では１～２ｋＶが好ましく、さらに好ましくは１．２～１．７ｋＶであり、窒素雰囲気では６～１１ｋＶが好ましく、さらに好ましくは７～８．５ｋＶである。

【００５５】また、プラズマ処理する際の周波数は、低すぎると基材と薄膜、又は、薄膜同士の密着性の向上が少なく、高すぎるとプラズマ密度が高くなり、基材又は薄膜が平滑に削られるため、基材と薄膜、又は、薄膜同士の密着性の向上が少なくなるので、アルゴン雰囲気、又は、窒素雰囲気では１～８ｋＨｚが好ましく、さらに好ましくは２～４ｋＨｚである。

【００５６】さらに、プラズマ処理に必要な時間は、短すぎると基材と薄膜、又は、薄膜同士の密着性の向上が少なく、長すぎると、基材又は薄膜が平滑に削られるため、基材と薄膜、又は、薄膜同士の密着性の向上が少なくなるので、アルゴン雰囲気、又は、窒素雰囲気では５～２０ｓｅｃが好ましい。

【００５７】（作用）本発明の表面処理品の製造方法は、少なくとも一方の対向面に固体誘電体が設置された対向電極間に処理用ガスを導入して、大気圧近傍の圧力となし、対向電極間にパルス化された電界を印加することにより、放電プラズマを発生させるとともに、前記対向電極間に設けられた基材をプラズマ処理する表面処理品の製造方法であって、２枚の基材を、それぞれ対峙された対向電極又は固体誘電体に密着させて、２枚の基材の間に処理用ガスを連続して導入するものであるから、処理用ガスが対向電極間に導入されて、大気圧近傍の圧力となされた状態で、パルス化された電界を印加して、安定化した高密度プラズマを発生させると同時に、対向電極に所定のパルス電界が印加されることにより、前記処理用ガスに依存した放電プラズマが発生し、この放電プラズマ中に設けられた２枚の基材に薄膜が形成される。

【００５８】又、高圧でプラズマ処理を行うことができるので、装置内は大気圧近傍の圧力下で処理が行われる。基材の導入口、排出口は、気体の漏れを許容しうる程度の機密状態にシールされていれば良く、真空系で行う処理のような大がかりな排気装置は必要としない。従って、基材の供給、基材の変更、ガス組成の変更が自由にでき、各種の表面処理品の製造を経済的に行うことができる。

【００５９】さらに、上記パルス化された電界の電圧立ち上がり時間が１００μｓ以下、電界強度が１～１００ｋＶ／ｃｍとすることにより、プラズマ発生空間中に存在する気体分子が、効率よく励起するとともに、アーク放電が発生することなしに、短時間の間に薄膜を形成することができる。

【００６０】

【発明の実施の形態】以下に本発明の実施の形態を図面を参照しつつ詳しく説明する。図３は本発明の表面処理品の製造方法に使用される装置の一例を示す模式図である。図３に示される様に、本発明に使用される装置は、主として、高電圧パルス電源部１０、１１、放電プラズマ処理装置２０、２１、巻出ロール８０、８１、及び引取ロール８２、８３から構成され、各放電プラズマ処理装置２０、２１は、平行平板型の対向電極（上部電極３０、３１、下部電極４０、４１）、処理用ガス供給部５０、５１、固体誘電体６０、６１、６２、６３、処理用ガス排出部７０、７１から構成されている。

【００６１】又、固体誘電体は６０、６１が上部電極３０、３１に、６２、６３が下部電極４０、４１に装着されている。

【００６２】各種の処理用ガス９０、９１は、放電プラズマ処理装置２０、２１の対向電極（即ち３０／４０、３１／４１）間に大気圧近傍の圧力下で、目的に応じて、任意の種類が選択されて導入され、各電極に上述の条件によるパルス化された電界が印加されて、処理用ガスの種類に応じた放電プラズマが発生させられ、これに上部電極３０、３１の固体誘電体６０、６１に基材１２が、下部電極４０、４１の固体誘電体６２、６３に基材１３がそれぞれ密着させられて、各種の薄膜が基材１２の下面及び基材１３の上面にそれぞれ堆積される。

【００６３】各放電プラズマ処理装置２０、２１に導入される処理用ガス９０、９１の種類は、前記したように、目的により異なり、同種であっても、異種であっても構わない。

【００６４】各放電プラズマ処理装置２０、２１には、隣接して加熱・冷却装置８４、８５が設けられ、基材１２、１３を所望の温度にできるようになっている。無論、放電プラズマ処理装置２０、２１に加熱・冷却機構を組み込み、温度制御可能としても構わない。

【００６５】放電プラズマ処理装置２０、２１はシール機構５２、５３、５４、５５によりシールされており、真空ポンプＰにより放電プラズマ処理装置２０、２１内を略真空状態に減圧状態にした後処理用ガス９０、９１を供給する。

【００６６】処理用ガス供給部５０、５１から供給され、対向電極（即ち３０／４０、３１／４１）間中に存在するガスは基材１２、１３間で層流を形成し、その流速が基材の処理幅にわたってほぼ均一であるのが好ましい。

【００６７】図４は処理用ガス供給部５０、５１の一例を示し、（Ａ）はその断面図、（Ｂ）はそのＡ－Ａ断面図である。

【００６８】直方形状の処理用ガス供給部５０の長手方向の一端部に、ガス供給管Ｇが接続されるガス導入口５６が設けられるとともに、長手方向に２つの室が設けられ、第１室５７にはガス導入方向に対向するように第１室５７の対角線上に斜板１４を設けられることにより、ガス導入口５６から遠ざかる程狭くなる区画を形成し、

ガス導入口５６から導入された反応ガスを乱流化し、その区画内での密度を略均一化させてその流速を略一様なものとすると同時に、その方向を偏向させた後、第１室５７の縁部近傍に設けた一様な多数の小孔群１５からガスを整流して吹き出す構造を有している。

【００６９】その小孔群１５から出たガスが導入される第２室５８を設けられ、その第２室５８内には、一端に一様な隙間２３を有する仕切り板２４を配置するとともに、縁部近傍に一様な幅のスリット２５を形成して、第１室５７の小孔群１５から出たガスが仕切り板２４を回り込んでスリット２５から層流となって放電空間に吹き出すように構成されている。これにより、小孔群１５から出たガスの流れが平均化される。

【００７０】なお、図３に示すように、高電圧パルス電源１０、１１は、各放電プラズマ処理装置の個々に独立した電源を使用しているが、共通の電源を用いてもよい。

【００７１】また、図３において放電プラズマ処理装置２０、２１のみ減圧にし、処理ガスで置換する例を示したが、巻出ロール８０、８１、引取ロール８２、８３、加熱・冷却装置８４、８５全てを減圧にし、処理ガスで置換してもよい。

【００７２】また、図３において基材１２、１３を別々の巻出ロール８０、８１より供給する例を示したが、巻出ロールを共通とし、放電プラズマ処理装置に導入する前に切断手段を設け、必要幅に切断した上で、対向電極（又は固体誘電体）の対向面にそれぞれ密着するように供給してもよい。

【００７３】

【実施例】以下、実施例を掲げて本発明を更に詳しく説明する。尚、以下の実施例では、高電圧パルス電源部１０、１１として（ハイデン研究所社製、半導体素子：ｉＸＹＳ社製、型番ｉＸＢＨ４０Ｎ１６０－６２７Ｇ）を用いた。

【００７４】図３に示した装置に於いて、処理用ガス供給部５０、５１として、図４に示したスリット状のガス吹き出し口を有するものを用い、表面処理品の製造装置とした。尚、放電プラズマ処理装置の上部電極３０、３１、下部電極４０、４１は、共に、幅３５０×長さ１５０ｍｍのＳＵＳ３０４製の平行平板型電極で、対向面に厚さ１．５ｍｍの酸化アルミニウム皮膜を溶射法でコーティングしたものを用いた。

【００７５】基材１２、１３は、厚み５０μｍ、幅３００ｍｍのポリエチレンテレフタレートフィルム（東レ社製、商品名「ルミラーＴ５０」）を使用し、２箇所の巻出ロール８０、８１から、上部電極３０、３１の固体誘電体６０、６１と、下部電極４０、４１の固体誘電体６２、６３に密着させ、連続的に上下とも０．５ｍ／ｍｉｎで走行させながら、供給した。

【００７６】次いで真空ポンプＰで放電プラズマ処理装置２０、２１内を０．１Ｔｏｒｒにした後、処理用ガス供給部５０から０．５体積％のテトライソープロポキシチタネートを含むアルゴンガス、処理用ガス供給部５１から０．５体積％のテトラエトキシシランと２０体積％の酸素ガスを含む窒素ガスを、共に１５ＳＬＭで供給し、略大気圧とした。

【００７７】次いで、上部電極３０、３１の固体誘電体６０、６１と、下部電極４０、４１の固体誘電体６２、６３間に、印加電圧４ｋＶ、周波数６ｋＨｚ、パルス電圧波形：図１（Ａ）、立ち上がり時間５μｓ、パルス幅２０μｓ、放電時間２０秒でプラズマ処理を行った。

【００７８】この結果、基材１２、１３の表面にＴｉＯ$_x$膜とＳｉＯ$_y$膜が形成された表面処理品１４、１５を得た。

【００７９】得られた表面処理品１４、１５の薄膜の屈折率、及び、膜厚をエリプソメーター（溝尻光学工業所社製、型式「ＥＶＡ－３６ＶＷ」）を用いて測定した。さらに、表面処理品１４、１５を任意にＡ４版に切断し、光干渉式自動膜厚測定装置（ナノメトリックスジャパン社製、型式「Ｍ－５１００」）を用いて５ｍｍ間隔に各薄膜の膜厚均一性を測定した。

【００８０】その結果、表面処理品１４、１５に形成されたＴｉＯ$_x$膜は、屈折率２．１３、膜厚９５ｎｍであり膜厚分布（Ｒ）は±３％であった。また、ＳｉＯ$_y$膜は、屈折率１．４４、膜厚１２８ｎｍであり膜厚分布（Ｒ）は±３％であった。

【００８１】次いで、得られた表面処理品１４、１５の反射率を、分光光度計（日立製作所社製、型式「Ｕ－３０００％）で測定したところ、可視光線平均（波長４００～７００ｎｍ）反射率は共に０．２％であり、ポリエチレンテレフタレートフィルム（７％）に比べて大幅に反射防止機能が付与された。また、処理面積は表面処理品１４、１５共に９ｍ^2／ｈｒであり、処理効率が、片面側のみの電極に基材を密着させた場合の２倍となった。

【００８２】

【発明の効果】本発明の表面処理品の製造方法は、上述のように構成されているので、大気圧近傍の圧力の下で、且つ、過大な設備投資を必要とせず、薄膜と基材との密着性に優れた表面処理品を効率よく製造し、又、プラズマ処理による堆積物が少なくてすむ。従って、本発明の製造方法を用いて、反射防止膜、光選択透過膜、赤外線反射膜、帯電防止膜、電磁波シール膜、半導体デバイス材料など各種機能膜の製造に利用できる。

【００８３】又、本発明の積層膜の連続製造装置は、従来の様に、減圧系にする必要がないので、大型の排気装置が不要であり、原料や製品の搬入・搬出が容易となるので、生産操業性、生産設備の経済性の点から、極めて有用である。

【図面の簡単な説明】

【図１】パルス電界の例を示す電圧波形図である。

【図２】パルス継続時間の説明図である。

【図３】本発明の表面処理品の製造方法に使用される装置の一例を示す模式図である。

【図４】処理用ガス供給部の一例を示し、（Ａ）はその断面図、（Ｂ）はそのＡ－Ａ断面図である。

【符号の説明】

１０．１１　高電圧パルス電源部

＊１２．１３　基材

１４．１５　表面処理品

２０．２１　放電プラズマ処理装置

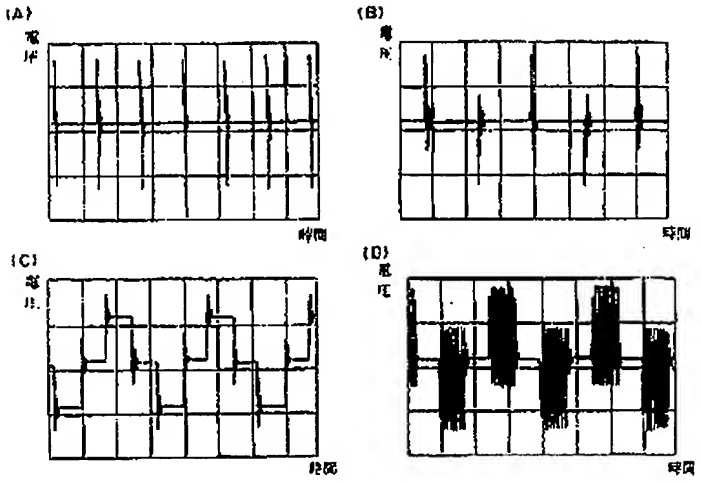
３０．３１　上部電極

４０．４１　下部電極

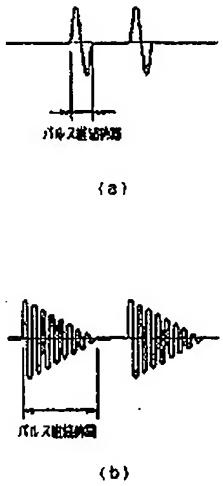
６０．６１、６２、６３　固体誘電体

＊　９０．９１　処理用ガス

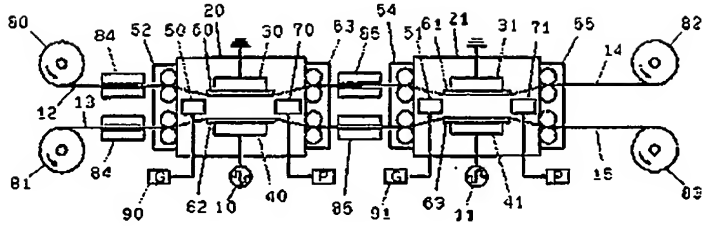
【図１】



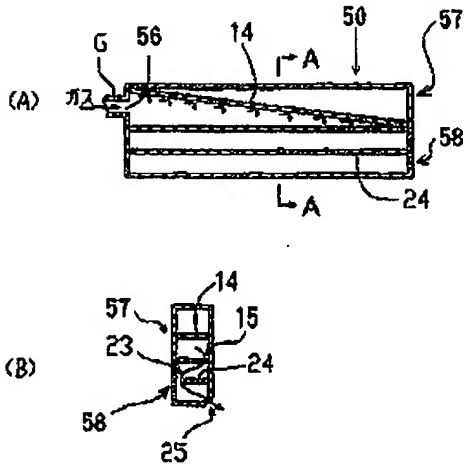
【図２】



【図３】



【図4】



フロントページの続き

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